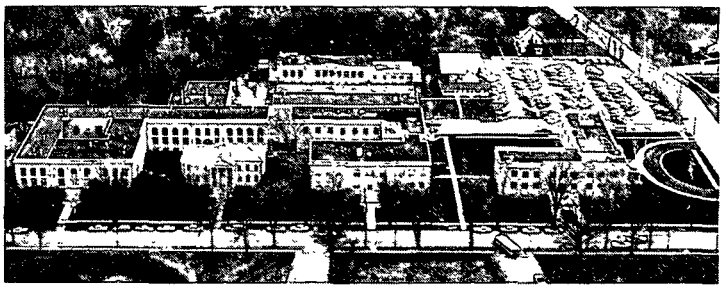

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A STRIP RESONANCE TECHNIQUE FOR MEASURING THE ULTRASONIC VISCOELASTIC PARAMETERS OF POLYMERIC SHEETS WITH APPLICATION TO CELLULOSE

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A Strip Resonance Technique for Measuring the Ultrasonic Viscoelastic Parameters of Polymeric Sheets with Application to Cellulose

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Portions of this work were used by BP as partial fulfillment of the requirements for the Ph.D. degree at The Institute of Paper Chemistry

A STRIP RESONANCE TECHNIQUE FOR MEASURING THE ULTRASONIC VISCOELASTIC PARAMETERS OF POLYMERIC SHEETS WITH APPLICATION TO CELLULOSE

B. Pankonin* and C. Habeger**

ABSTRACT

An acoustic strip resonance apparatus that measures the viscoelastic response of polymeric sheets over the temperature range of 100-400°K and at frequencies from 20 to 100 kHz is described. This is a computer controlled instrument which uses the resonant frequency and the quality factor of standing waves in strips to calculate the ratio of complex Young's modulus to density. Results are presented for cellophane and paper samples. These are consistent with measurements reported by others at lower frequencies. That is, (a) a single predominant secondary relaxation process which corresponds to the γ relaxation occurring at 200°K and 1 Hz is found in dry samples at 260°K and 60 kHz, (b) as moisture is added, the γ relaxation weakens and a higher temperature, β, relaxation appears, and (c) at low temperature, moisture addition initially increases the mass specific Young's modulus. The effects of methanol on the viscoelastic parameters of cellulose were also measured and found to be similar to those of water.

INTRODUCTION

Cellulose is a naturally occurring polymer and is the most abundant chemical species found in paper products. As a viscoelastic polymer, cellulose exhibits time and temperature dependent mechanical properties which are the result of molecular level relaxation processes. Understanding these relaxation processes is central to understanding the linear mechanical response of wood pulp fibers and paper during manufacture and use.

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The temperature and moisture dependencies of the secondary relaxations in cellulose have been studied with various dynamic mechanical and dielectric methods (1-3). At frequencies from 1 to 10 Hz, the torsion pendulum has been used to measure the shear moduli of cellulose sheets and single wood fibers (4-6). Reovibron data are reported from 10^{-2} to 10^{2} Hz (7-11). Vibrating reed measurements have been made from 40 to 700 Hz (12,13). Above 1 kHz, the study of relaxation phenomena in cellulose has been carried out for the most part with dielectric techniques (4,13-15). Since the molecular motions in cellulosics which are responsible for mechanical relaxations involve groups that are also dielectrically active, dielectric and mechanical measurements are sensitive to the same processes. However, the magnitude of mechanical relaxations can be found only by direct measurement, and there is a fundamental need for methods which detect high frequency viscoelastic responses. Since ultrasonic velocity measurements are important in the nondestructive evaluation of paper stiffness [both on-line (16) and in the laboratory (17-19)], there are practical reasons to improve our understanding of mechanical relaxations in cellulose at high frequencies.

In cellulosics, two secondary relaxations are observed below room temperature at low frequencies (~ 1 Hz): the β relaxation at about 250°K and the γ relaxation at about 180°K. Moisture plays a principal role in these relaxation processes. In dry cellulose, the γ relaxation is large and the β is absent. However, as moisture is added, the β relaxation appears and strengthens relative to the γ relaxation (5,10). The presence of moisture shifts both relaxations to lower temperatures, suggesting water acts as a plasticizer for both processes. The simultaneous increase in the β relaxation amplitude and decrease in the γ relaxation amplitude with moisture is consistent with the

hypothesis that moisture is converting γ sites to β sites. Bradley and Carr (10) believe that the γ relaxation is a hindered conformation change (rotation) of the methylol groups in the disordered regions of cellulose. They attribute the β relaxation to rotation of methylol-water complexes, also in the disordered areas.

INSTRUMENT DESIGN AND CONSTRUCTION

The instrument is used to characterize the mechanical resonances of a test strip coupled between a pair of ceramic piezoelectric transducers. As in Fig. 1, one transducer, the transmitter, is excited with a continuous sinusoidal wave from a Hewlett Packard 3325A Frequency Synthesizer. Longitudinal vibrations are excited in the test strip through a transverse expansion mode motion of the transmitter. The vibrations in the strip create a small signal in a receiving transducer. The receiver is the input for an Ithaco 393 Lock-In Amplifier whose reference frequency is the same as the excitation signal. The lock-in output goes to an analog input of a Texas Instruments 9900 Microcomputer. The microcomputer, which controls the frequency synthesizer over an IEEE bus, adjusts the excitation frequency and records the corresponding lock-in output. The transducer-test strip assembly is housed in a glass environmental chamber. A sample temperature signal is generated by a thermocouple placed near the sample. The signal is conditioned by a Digitec HT 2780, and digitized in the computer. The temperature reading is accurate to 0.20°K between 75 and 373°K. The moisture content of the test strip is inferred by weighing a separate sample supported by a quartz spring balance, also inside the chamber. Spring displacement is visually monitored using a telescope outside the chamber. The results of a resonance characterization can be printed out directly, graphed by an X-Y plotter, or sent to a main-frame computer over a modem.

Figure 1 here

The most important part of the development of this instrument is the design and construction of the transducers-sample holder assembly. The combination of transducers and test strip must resonate in modes that are simply related to the viscoelastic properties of the sample. Excitation of spurious modes in the transducers or in their mounts must be suppressed. The transducers are made from a 0.10-inch-thick sheet of piezoelectric ceramic (Edo Western EC-65 PZT). The ceramic is polarized in the thickness direction and electrodes are provided on the top and bottom. The ceramic sheet is cut with a carborundum wheel into rectangles about 0.25 inch by 0.25 inch to form the transducers. These dimensions are small enough to ensure that all resonances in the ceramic blocks are over 200 kHz, which is well above the 10 kHz to 100 kHz operating range of the instrument. Electrical contact is made by soldering the ground and active leads of a miniature coaxial cable to opposite electrodes of a transducer. The cable is threaded through a hole in an aluminum block and is held near the transducer by filling the hole with a high loss silicone potting compound (G.E. RTV 615). The potting compound acoustically isolates the transducers from the mounting frame. The isolation is considered to be sufficient, since the maximum response of the lock-in amplifier with no sample in place is more than 40 db below a typical strip response at resonance. The aluminum blocks are mounted on a track, which permits the separation of the transducers to be adjusted. Figure 2 is a schematic diagram of the transducer-sample holder assembly.

Figure 2 here

Test strips are cut with a razor blade using a stainless steel template. The samples are 0.2 cm wide and from 4.0 to 7.0 cm long. The test strips are

coupled to the transducer with epoxy (Miller/Stephenson 907). A thin layer of epoxy is metered onto a 0.25-inch by 0.10-inch face of the transducers. The test strip is arched between two transducers as shown in Fig. 2 and the epoxy is allowed to cure for 12 hours. Arching the test strip between the transducers reduces the stresses that arise from moisture and temperature induced length changes of the strip.

The vibrations excited by the instrument are primarily longitudinal motions in the strip and the transducers. The measured resonant frequencies are near those of longitudinal motion in a test strip with fixed ends; however, interactions with transducers lead to small shifts. The following analysis of these frequency shifts demonstrates that they decrease as the order of the harmonic increases and that (with the exception of the fundamental resonance) the resonance condition is very nearly that the strip is an integral number of half wavelengths long.

The effect of the transducers on the resonance condition can be estimated by repeated application of the transmission line impedance transfer equation. That is, if the impedance, Z_o, is known at one point on a transmission line, the impedance at a distance, ℓ, from the point is

$$Z = W\,(Z_o + iW \tan k\ell)/(iZ_o \tan k\ell + W), \qquad (1)$$

where W is the specific impedance of the transmission line, i is the square root of -1, and k equals the angular frequency divided by the sound velocity in the line. To find the resonance condition, the impedance of the transducer-sample system is calculated by starting with zero impedance at a far end of a transducer and using Eq. (1) to transfer to the strip, then to transfer through the

strip to the second transducer, and finally to transfer to the outer edge of the second transducer. The resonance condition is that this impedance equal zero. The result is

$$\tan k_s \ell_s = 2 \tan k_t \ell_t / \left(\frac{Z_t}{Z_s} \tan^2 k_t \ell_t - \frac{Z_s}{Z_t}\right), \qquad (2)$$

where the s subscript denotes the test strip and t denotes the transducers. The ratio, Z_t/Z_s, represents the effective impedance ratio of the transducer to the test sample. Since the transducer area on the coupling surface is considerably greater than that of the sample, since force continuity is maintained at the interface, and since the transducer deformation must vary over the coupling surface, Z_t/Z_s is between the ratio of the specific impedances and the ratio of the areas times the specific impedance. Using typical values, this means that $10 < Z_t/Z_s < 500$. Notice that as $(Z_t/Z_s) \tan k_t \ell_t$ becomes large the resonant condition approaches the requirement that the test strip length is an integral number of half wavelengths ($\tan k_s \ell_s = 0$ or $k_s \ell_s = n\pi$). The length of the test strip is normally cut so that the first three resonances are at about 30, 60, and 90 kHz, respectively. At these frequencies, the values of $\tan k_t \ell_t$ are approximately 0.36, 0.82, and 1.65. Therefore, from Eq. (2), the magnitude of the frequency shift caused by the transducers is roughly decreasing linearly with frequency and the relative correction is decreasing as the frequency squared. Inserting typical values into Eq. (2) shows that the error from assuming that the resonant condition is $k_s \ell_s = n\pi$ is a few percent for the fundamental at 30 kHz, less than a percent for a 1st harmonic at 60 kHz, and very small for the second harmonic. This means that the resonant frequencies should be unevenly spaced, the fundamental being a few percent larger than one half the 1st harmonic, and the 1st harmonic being slightly larger than 2/3 the 2nd harmonic. This trend is observed experimentally; the fundamental is normally from

3 to 6 percent greater than half the 1st harmonic while the difference between 1/2 the 1st harmonic and 1/3 the 2nd harmonic is within experimental error. This is taken to mean that the $k_s \ell_s = n\pi$ condition is a good approximation for the resonance condition of the harmonics but not of the fundamental.

One way to exhibit the resonance characteristics of the strip is to (a) slowly sweep the frequency of the synthesizer from 10 kHz to 110 kHz, (b) apply the amplitude output of the lock-in amplifier to the Y axis of the X-Y recorder, and (c) put an analog signal from the synthesizer which is proportional to the frequency on the X-axis. A typical result is the spectrum shown in Fig. 3. Notice that the peaks are sharp and almost equally spaced. When the strip is improperly coupled to the transducers, shoulders develop on the peaks; therefore, the appearance of well formed peaks (as in Fig. 3) is the test for proper bonding. This test is routinely performed as temperature or moisture is varying to check for debonding.

Figure 3 here

Once it is verified from the X-Y recorder trace that the sample is properly bonded, the computer is allowed to control the frequency synthesizer and determine the real part of the mass specific Young's modulus, E/ρ, and the loss tangent, $\tan \delta$, of the strip. With the exception of the fundamental mode, $(E/\rho)^{1/2}$ is (to first order in $\tan \delta$) equal to $2\ell_s f_{max}/(m+1)$, where f_{max} is the frequency of a maximum lock-in response and m is the order of the harmonic. Assuming all losses occur within the strip, $\tan \delta$ to first order is $\Delta f/f_{max}$, where Δf is the frequency width of the peak at one over the square root of 2 of the maximum amplitude. This is valid for the fundamental and the harmonics. In

fact, there is less peak overlap on the fundamental and it is considered to be the best peak for loss tangent measurements. To determine f_{max} and Δf, the computer first establishes a baseline for the peak by searching the shoulders until it finds the minimum response on each side of the peak. Subsequent amplitudes are taken relative to a baseline constructed between these two minima. Using an optimization routine the computer next finds the frequency of maximum response to ± 5 Hz and calculates the mass specific modulus at that frequency. The peak width is found by measuring the response at four frequencies near the half height on both sides of the peak. A least squares line is calculated for both sets of points and Δf is determined to a resolution of about 30 Hz. Figure 4 demonstrates the specific modulus and loss tangent calculation for a typical 1st harmonic resonance. The computer continually repeats this process at a rate of about 3 cycles a minute. After each cycle, it prints out and sends to a host computer values of f_{max}, E/ρ, tan δ, and the temperature. The strip moisture content is periodically determined from the location of the quartz spring suspending the weighing sample.

Figure 4 here

The sample length used by the computer to calculate specific modulus is the room temperature value at the moisture content of the test. This means that length variations due to temperature changes are not taken into account. Measurements of arc depth in our apparatus and data from Klason and Kubat (4) indicate that a 3% length increase from 100 to 400°K should be expected. This is about one tenth of the change in velocity over the same temperature range; therefore, ignoring thermal expansivity leads to small but not insignificant errors. This, of course, has no effect of loss tangent values, as their determination is length independent.

The environmental chamber is a glass tube. In the bottom of the tube is a frame with two transducer-strip assemblies which can be alternately switched into the instrument by the computer using coaxial relays. A weighing sample suspended from a quartz spring is just above the test frame. The portion of the tube containing the frame and weighing sample is surrounded by a Dewar flask. A nichrome wire is wrapped around the tube for heating, while cooling is accomplished by forcing liquid nitrogen vapor into the gap between the tube and the Dewar. The temperature is controlled by changing the flow rate of the nitrogen vapor or the heating wire current. By these means, the sample temperature can be varied from 100 to 380°K. The tube can be evacuated by opening a valve to a vacuum pump, dry air can be provided from a six foot column full of "Drierite®" desiccant, or the tube can be opened to the external environment which is controlled at 72°F and 50% RH.

RESULTS AND DISCUSSION

Viscoelastic parameters measured by the strip resonance technique are reported for two samples. They are a bleached kraft paper handsheet and a commercial cellophane. The cellophane was obtained from E. I. du Pont de Nemours and Co., Inc. It was unplasticized and about 38 μm thick (PUDO-134). The paper sample was a Canadian spruce pulp handsheet. The screened yield was 47% and the kappa number was 34.8. Bleaching conditions were DED and the bleached pulp brightness was 80.0. The pulp was beaten 7500 revolutions in a PFI mill. The sample thickness is 64 μm, and the 50% RH density is 0.94 g/cm^3.

Figure 5 is a plot of the specific modulus and loss tangent of the cellophane as a function of temperature. The sample was conditioned at a temperature of 370°K and a pressure of 0.2 torr for one hour prior to testing.

average of the two phases and the CD more of a series average (20). The stiffer, less lossy crystalline phase is more important in the MD; therefore, the MD has a larger modulus and a smaller loss tangent. Finally, notice that the MD fundamental loss tangent maximum is at a higher temperature than the MD first harmonic. This is consistent with the standard theories of the time-temperature behavior of thermally activated relaxations in polymers (1-3).

The thermal relaxation in dry cellulose, observed using the resonant strip technique at about 260°K and 60 kHz, is assumed to be the γ relaxation reported by many others (5-15). Figure 6 is an Arrhenius plot of the frequency and temperature of the loss tangent maxima for strip resonance and literature results considered to be taken at very low moisture contents. The parallelogram in Figure 6 encloses the strip resonance data gathered for dry cellophane and bleached kraft paper. All the data fall near a straight line with an activation energy of about 12 kcal/mole.

Figure 6 here

After the cellophane data reported in Fig. 5 were taken, the samples were subjected to a more severe drying condition (380°K and 0.2 torr for 1 hour) and retested. There was a 0.2% decrease in sample weight during the 380°K conditioning; therefore, referenced to the driest state, the moisture content during Fig. 5 testing was 0.2%. Figure 7 is a comparison of the MD first harmonic moduli and loss tangents for the two drying procedures. The first test produced a greater loss tangent maximum, indicating that moisture is reducing the magnitude of the γ relaxation. This is consistent with the results of Bradley and Carr (10) for cellulose and cellulose derivatives and with the antiplasticizing action of water on the γ relaxation in nylon reported by Starkweather (23). The

specific modulus results are not considered to be significantly different; however, later it will be shown that water increases the mass specific modulus at low temperatures and low moisture contents.

Figure 7 here

Klason and Kubat (4) presented evidence that the γ transition temperature is independent of cellulose modification (~ 200°K at 1 Hz). In addition, Bradley and Carr found similar transition temperatures for cellophane and amylose, a cellulose derivative. Moreover, they showed that the γ relaxation magnitude in amylose decreased as crystallinity increased, suggesting that the γ relaxation occurs in the amorphous regions. This leads us to expect that the strip resonance loss tangent will peak at the same temperature for dry cellophane and dry paper, and that the cellophane, with its larger amorphous content, will have a stronger relaxation. The data in Fig. 8 confirm these expectations: the γ transitions occur at a common temperature; the cellophane maximum is higher and broader; and the cellophane exhibits a greater relative change in modulus with temperature.

Figure 8 here

The specific Young's modulus and loss tangents were also measured as a function of temperature at higher moisture contents. To do this, the sample was first equilibrated to the desired moisture content at room temperature. The environmental chamber was then sealed and data were taken as the temperature decreased. As observed in the weighing sample, there initially was a small increase in moisture as temperature fell; however, below 250°K the moisture content was stable. Calculations of the MD first harmonic specific moduli are

presented in Fig. 9. The listed moisture contents are the values at room temperature. The values below 250°K are 14, 10, 5.5, 2.5, and 0%. The interesting feature here is that moisture increases specific modulus at low temperature and decreases modulus near room temperature. This antiplasticizing action of water at low moisture contents has been observed by progressive drying and moistening of the sample, showing that it is not caused by irreversible changes in the sample. Similar results are reported by Bradley and Carr (10) at about 1 Hz. They attribute the effect to the combined action of the γ transition and a β transition. The β transition, which is absent in dry cellulose, is at a higher temperature than the γ transition. It also has a higher activation energy (~ 16.5 kcal/mole) than the γ transition. As moisture is added both the γ and β transitions move to lower temperatures, but the β is enhanced while the γ weakens. At low temperature (below the β transition) moisture tends to increase specific modulus as it inhibits the γ transition. Near room temperature the water induced increases in the β transition dominate and the modulus decreases with moisture. At about 3% moisture Bradley and Carr see distinct loss tangent peaks for the γ and β relaxations. Since the β transition has a higher activation energy than the γ, the two transitions are closer together at ultrasonic frequencies. Therefore, the combination of γ and β transitions produced a single broad maximum in the strip resonance loss tangent curves for all moisture contents studied. For cello-phane, Bradley and Carr find a modulus crossover temperature for 0.34% water and 7.3% water at about 170°K. Judging from Fig. 9, the corresponding crossover would be at about 240°K for the strip resonance measurements. The strip resonance experiment operates at four orders of magnitude higher frequency, and viscoelastic processes occur at higher temperature as frequency increases.

Figure 9 here

An influence of moisture on the secondary relaxations is demonstrated in Fig. 10, where the temperature of the loss tangent peak is plotted vs. moisture content for the MD fundamental and the MD first harmonic resonance of cellophane. At low moisture content, moisture increases the magnitude of the higher temperature β transition at the expense of the γ, and the temperature of the observed maximum goes up with moisture. At higher moisture contents the β transition dominates, and the data reflect its natural decrease in temperature with moisture. The fundamental and first harmonic results show the same trends. The increase in the temperature of the maximum in the loss tangent with frequency is consistent with the normal behavior of viscoelastic relaxations.

Figure 10 here

The effect of methanol on the viscoelastic parameters was found to be remarkably similar to that of water. Figure 11 is a graph of the mass specific modulus of cellophane vs. methanol content. Notice that the crossovers are still evident; methanol also inhibits the γ transition and enhances the β transition. Possibly, its larger size causes methanol to be a more effective plasticizer than water, when compared at equal molar concentrations.

Figure 11 here

ACKNOWLEDGMENT

Portions of this work were used by B.P. as partial fulfillment of the requirements for the Ph.D. degree at The Institute of Paper Chemistry.

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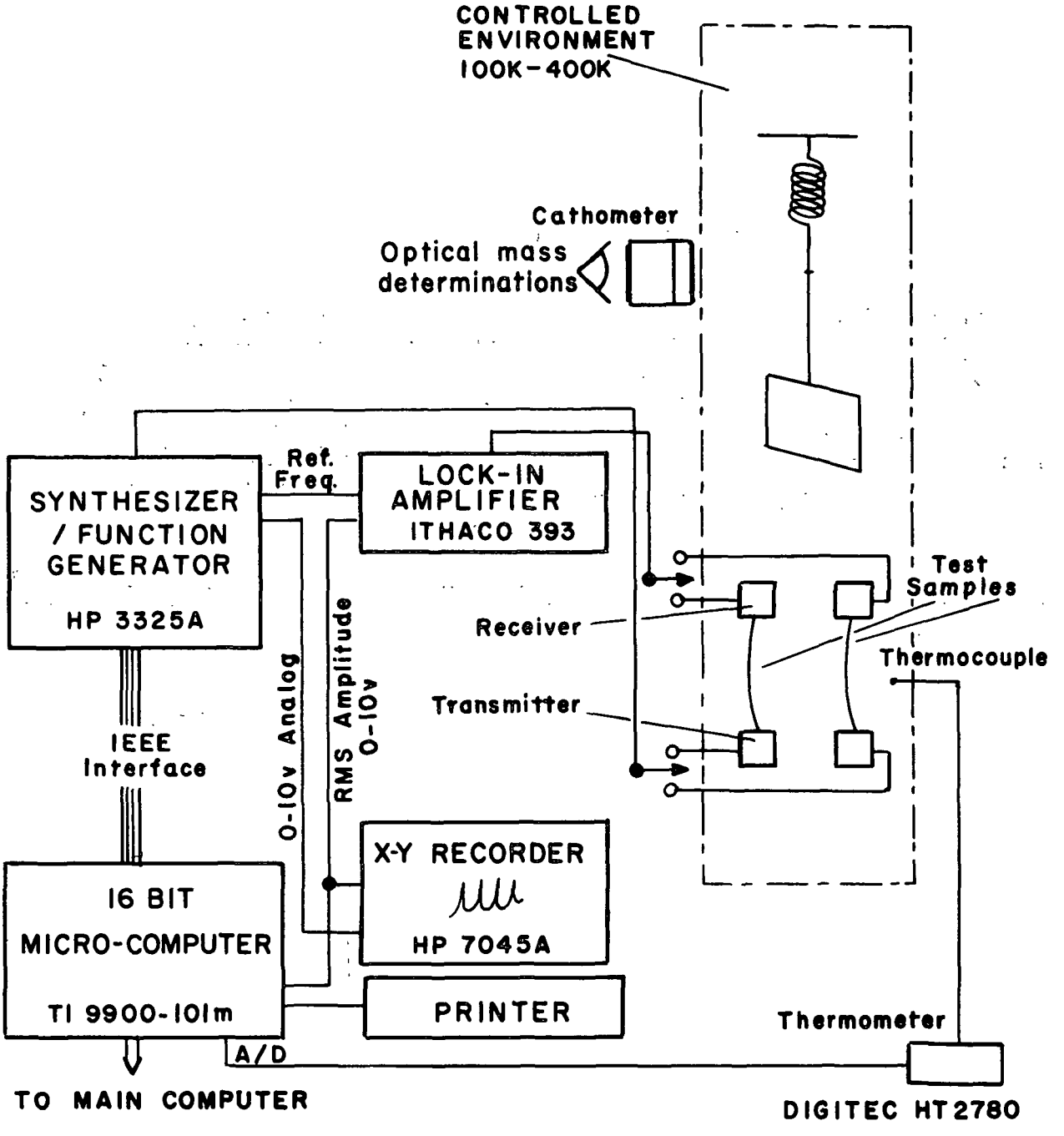

Figure 1. Overall schematic of the strip resonance technique.

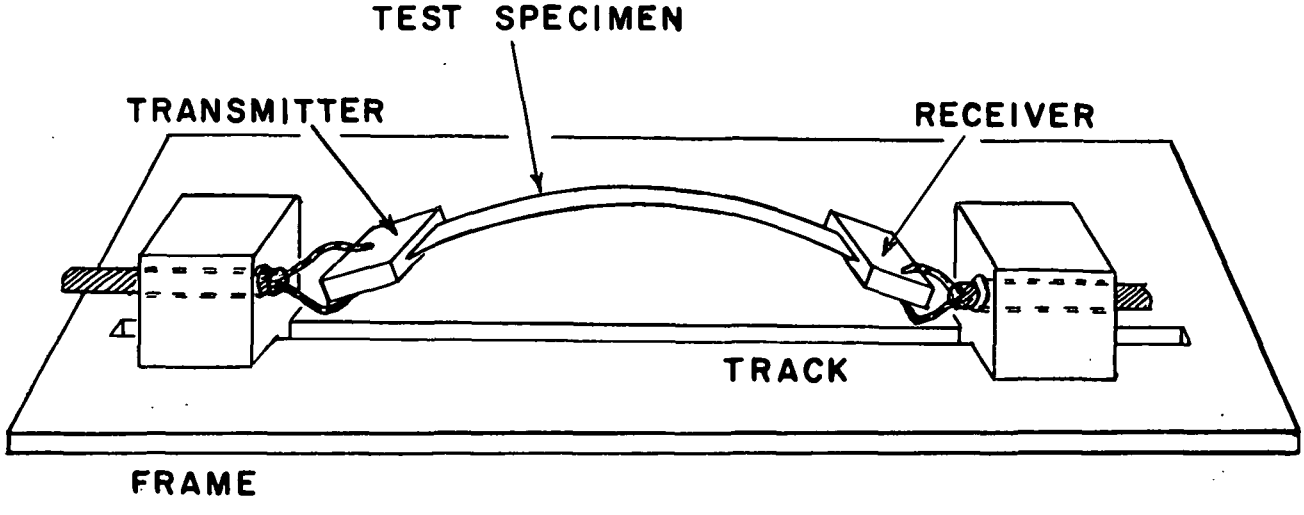

Figure 2. Schematic of the transducer-sample holder assembly.

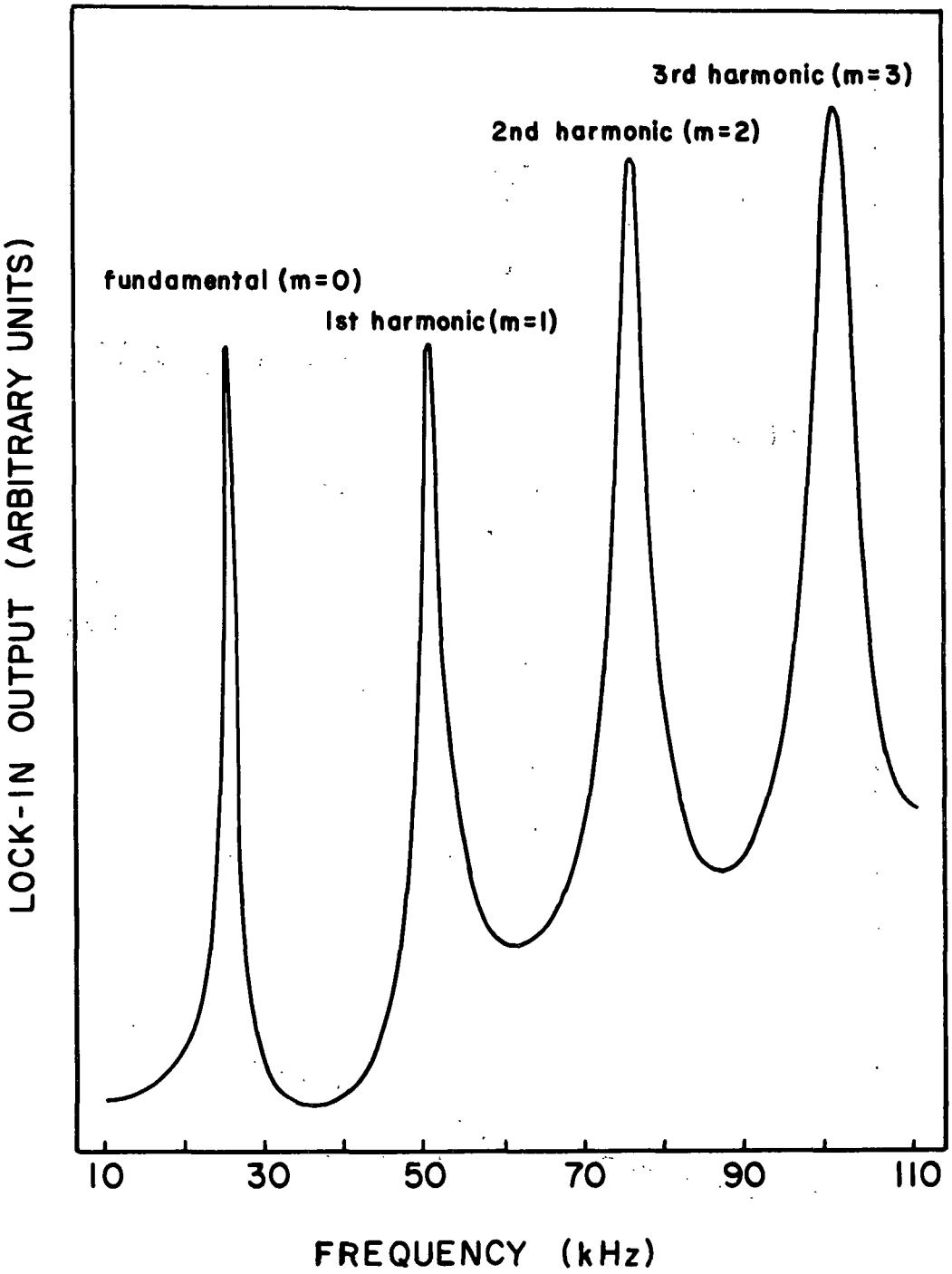

Figure 3. A typical X-Y recorder plot of the lock-in amplifier response vs. frequency.

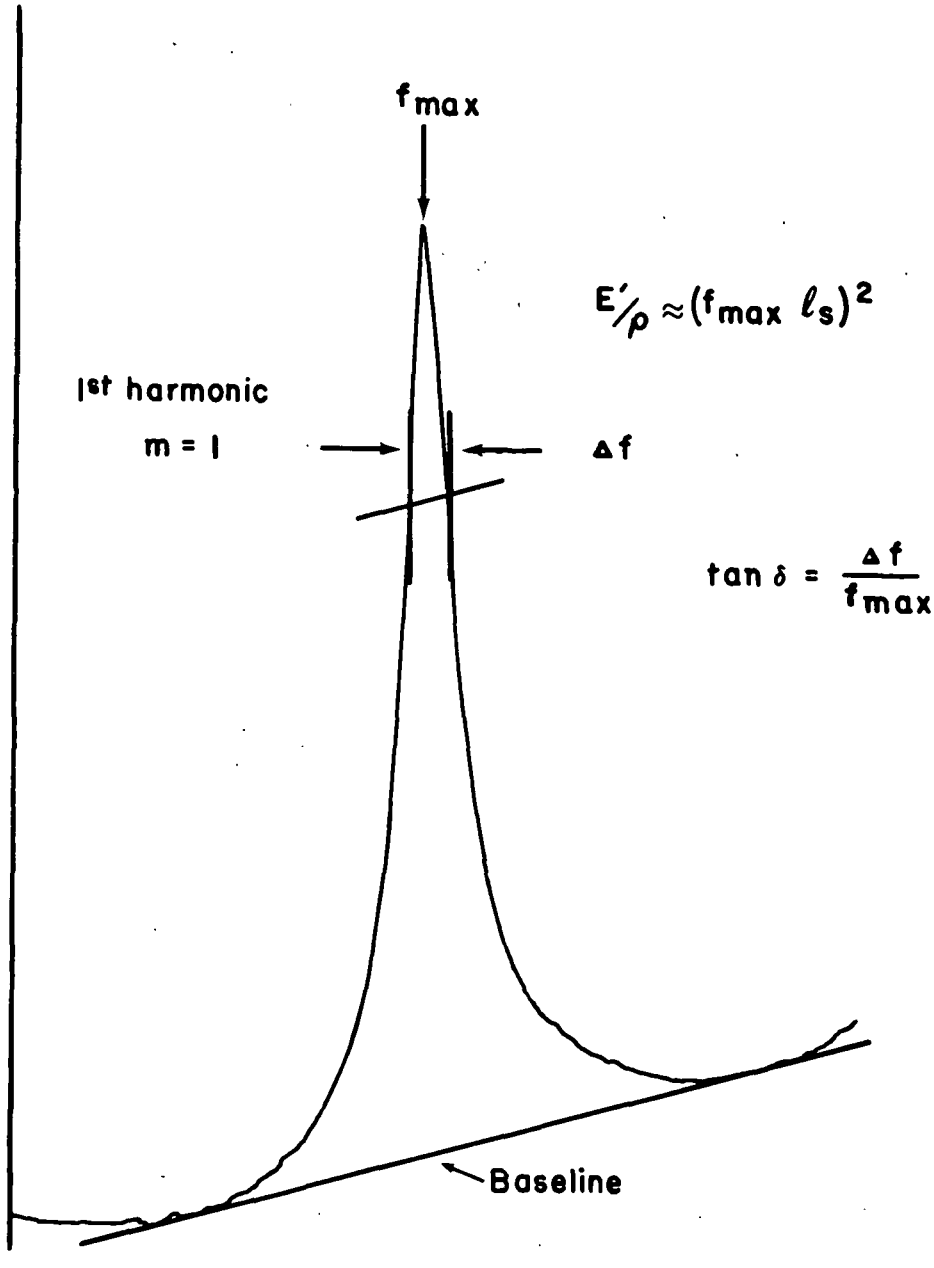

Figure 4. The determination of modulus and loss tangent from a resonance peak.

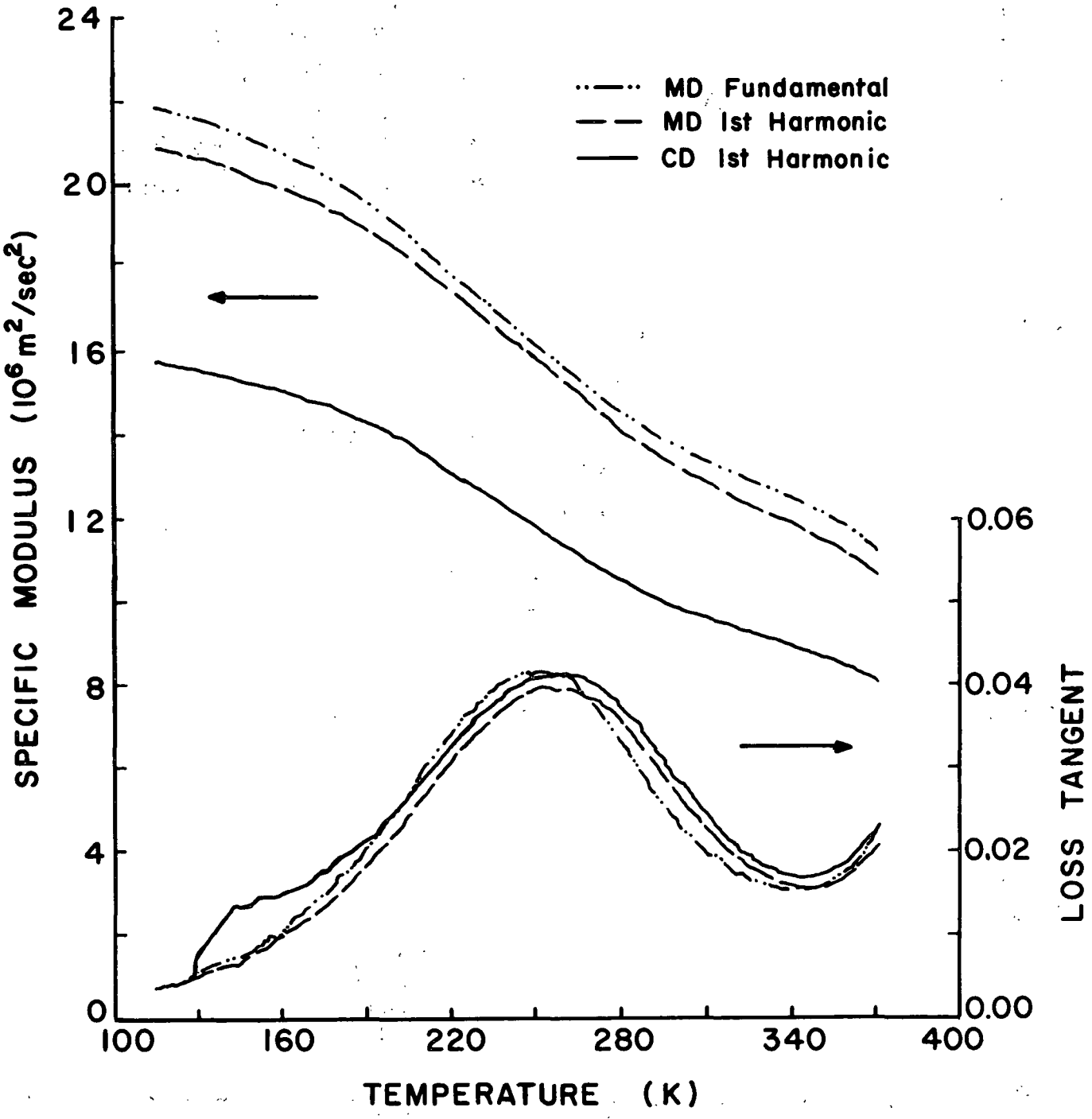

Figure 5. Loss tangent and specific modulus vs. temperature for cellophane dried at 370°K, 0.2 torr for 1 hour. MD fundamental (~ 30 kHz), MD first harmonic (~ 60 kHz), and CD fundamental (~ 60 kHz) data are present.

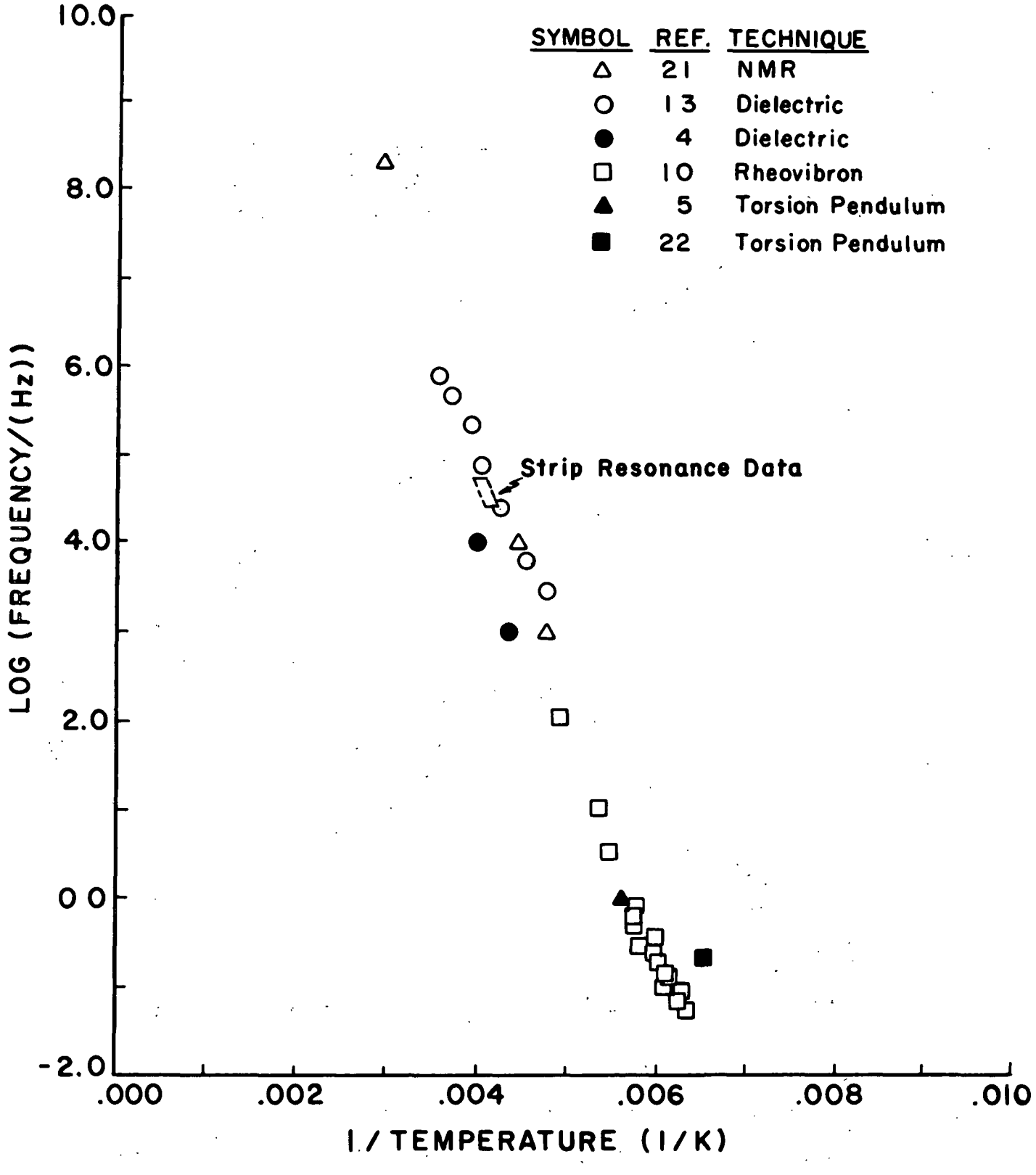

Figure 6. Literature and strip resonance log frequency vs. inverse temperature for loss tangent maxima in the γ transition.

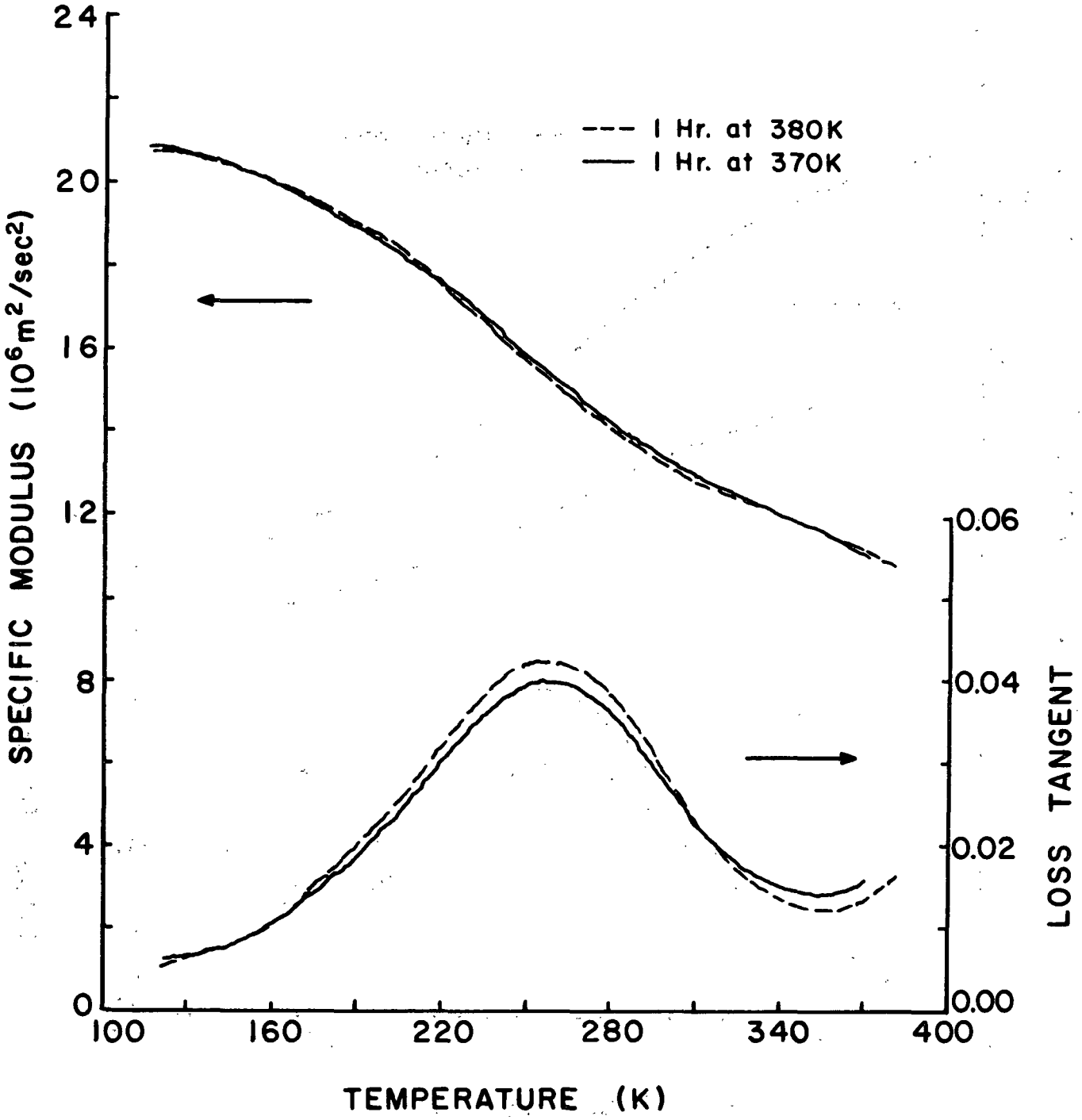

Figure 7. MD loss tangent and specific modulus vs. temperature for a cellophane sample dried at 370°K and at 380°K with 0.2 torr for 1.0 hour.

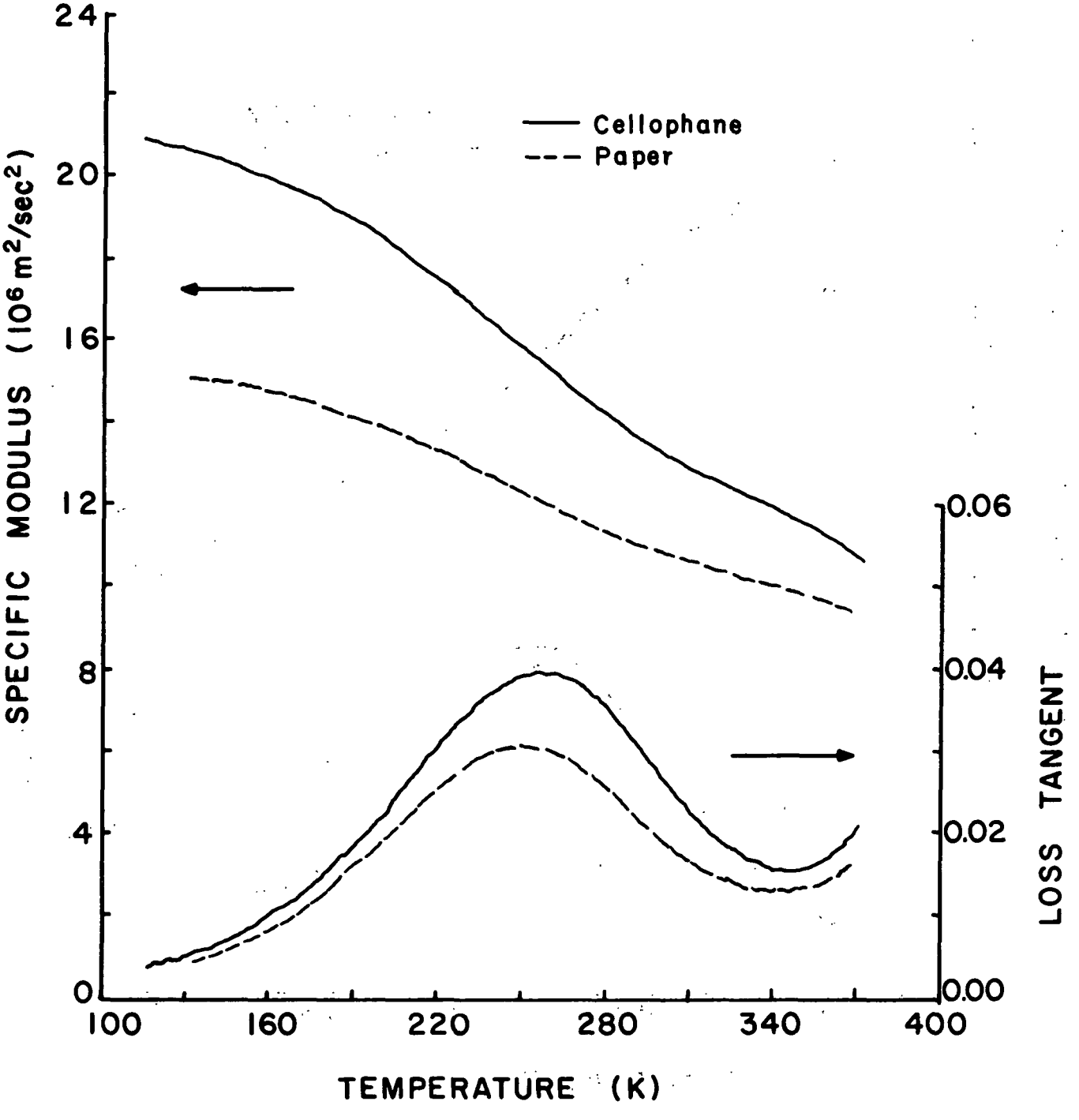

Figure 8. MD loss tangent and specific modulus vs. temperature for dry cellophane and dry paper dried at 370°K.

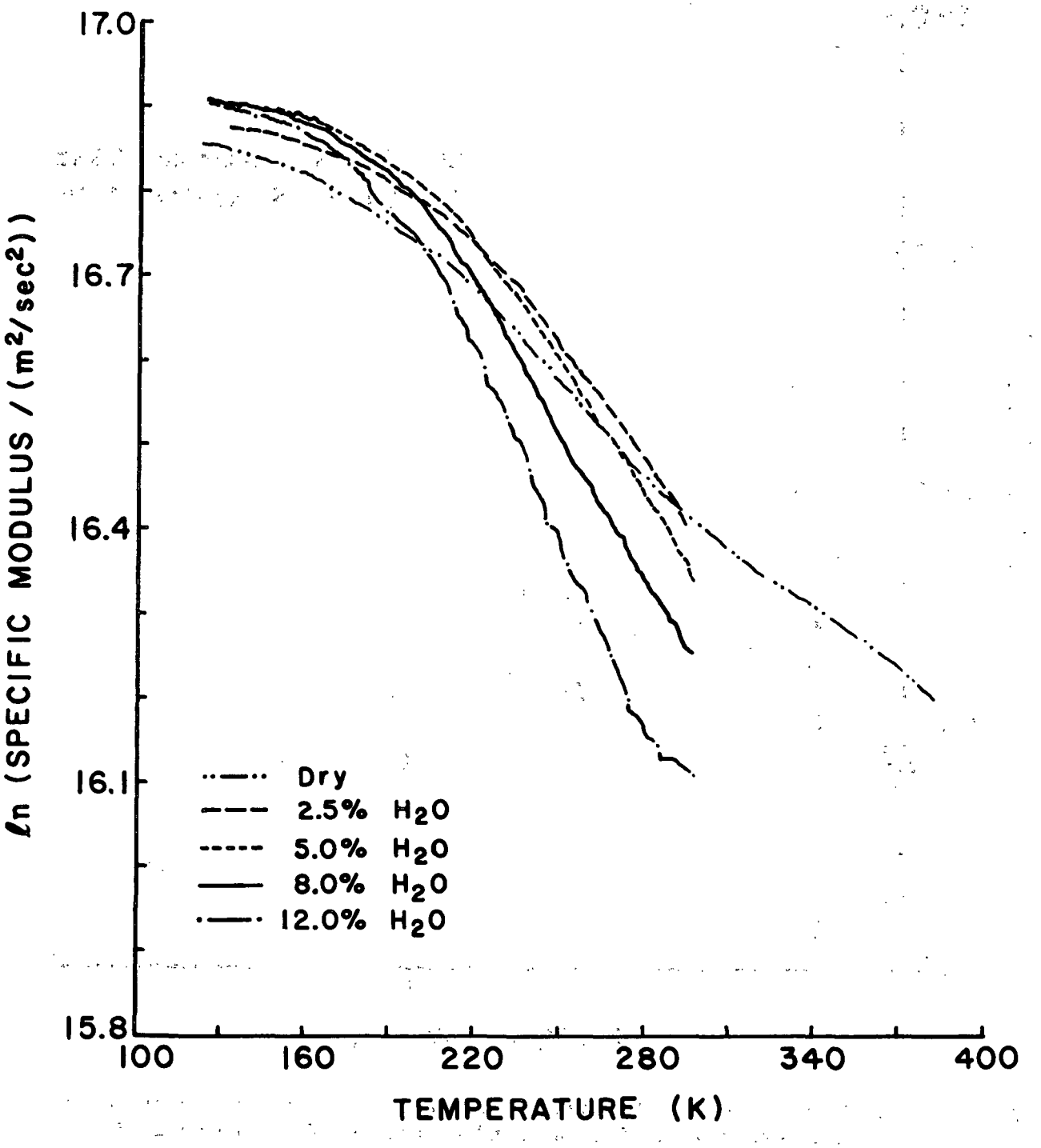

Figure 9. The effect of water on the natural log of specific modulus vs. temperature plot for cellophane.

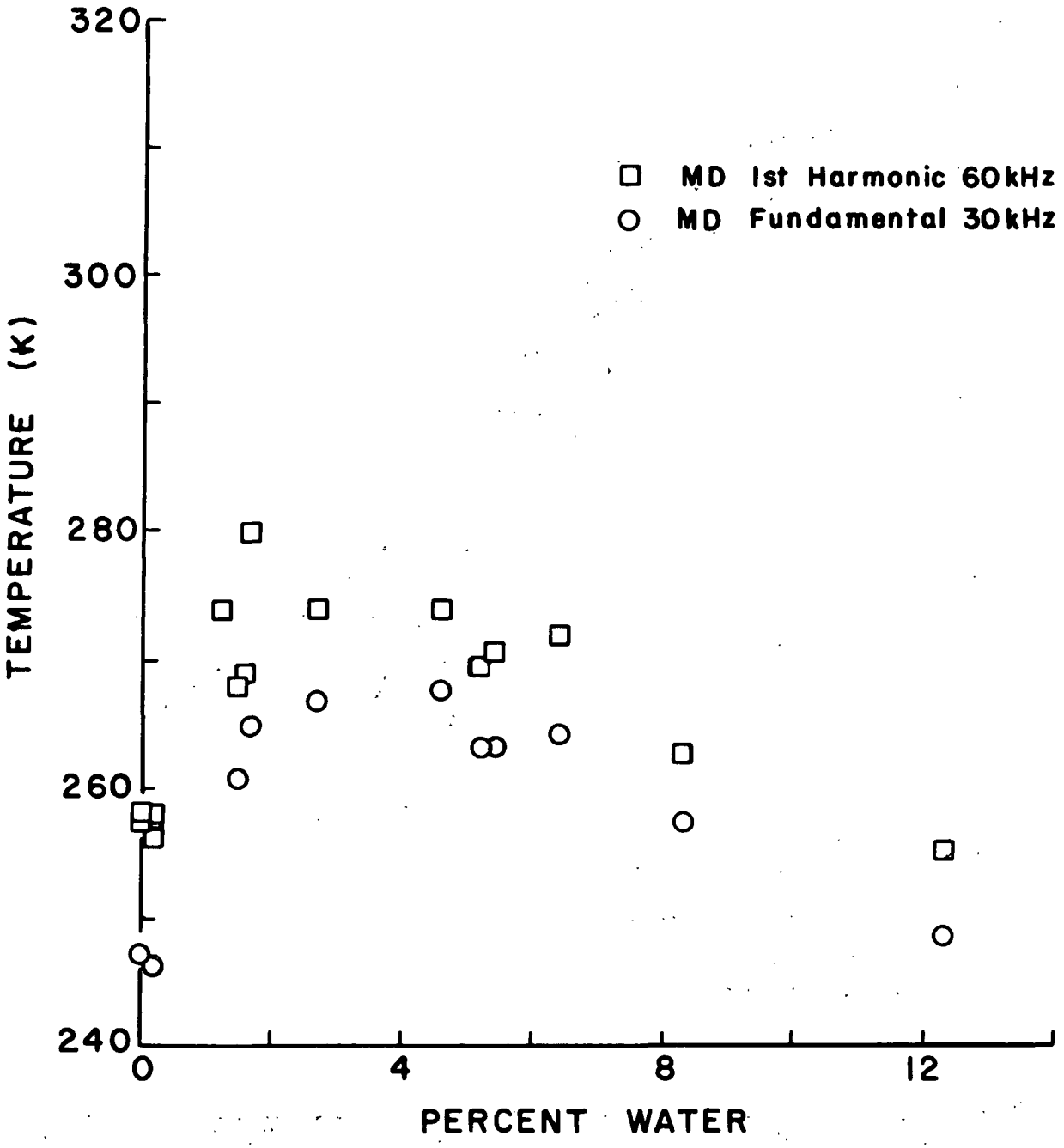

Figure 10. The temperature of the maximum in the loss tangent-temperature plot vs. moisture content for the fundamental and first harmonic in cellophane.

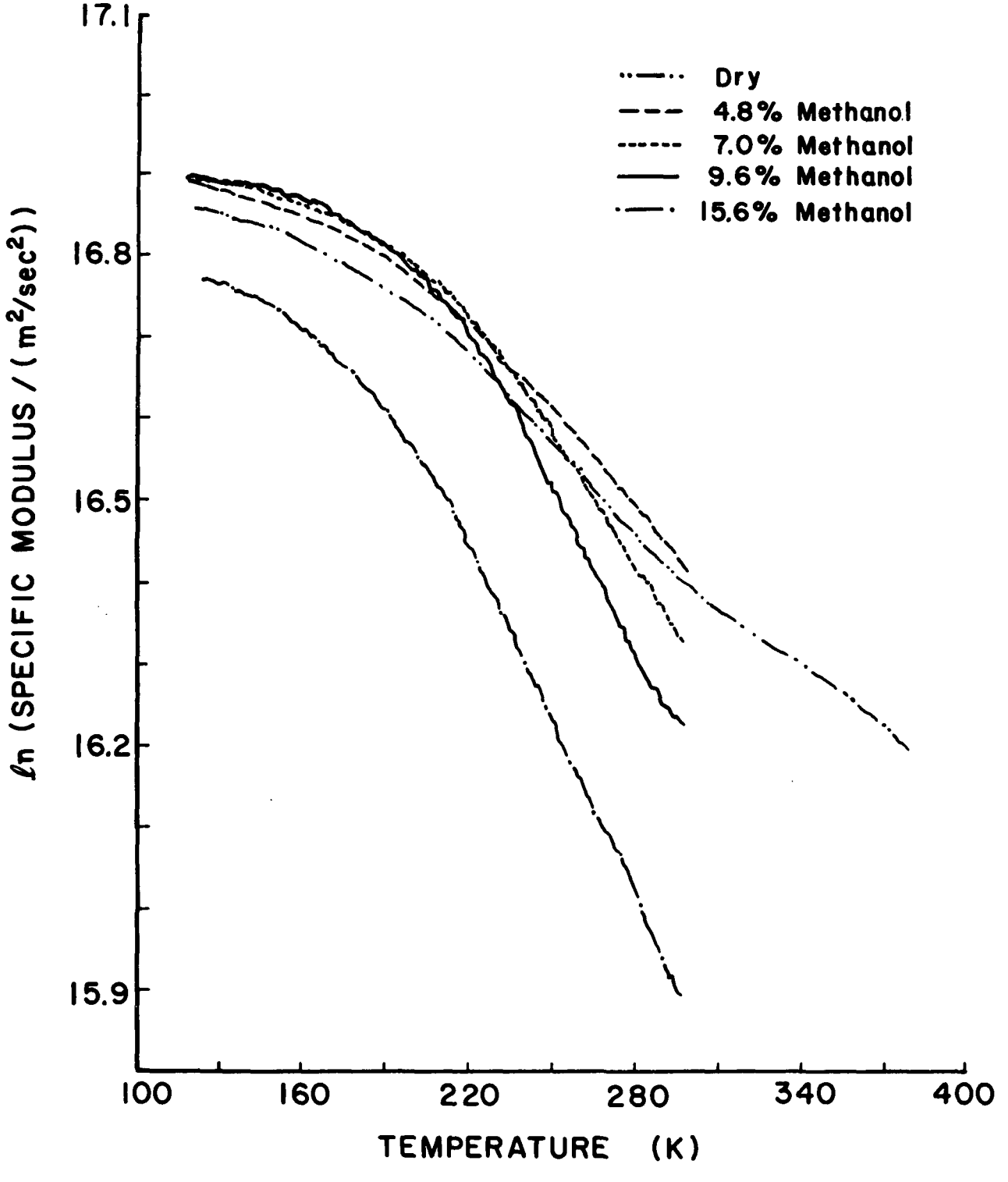

Figure 11. The effect of methanol on the natural log of specific modulus vs. temperature plot for cellophane.